
QUANTITATIVE ANALYSIS BY COMPREHENSIVE BIDIMENSIONAL GAS CHROMATOGRAPHY USING INTERVAL MULTI-WAY PARTIAL LEAST SQUARES CALIBRATION

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There are two basic approaches for quantitative analysis by GC×GC. Several users utilize already available integration software, which has the advantage of being accessible to virtually all analytical laboratories using GC. Yet, for many reasons multivariate chemometric tools seem to be much more convenient to process GC×GC data. When performing the individual quantitation of target analytes, use of conventional integration software would customarily demand either customisation of the program (which is generally impossible to most users) or manually finding and adding up the integrated areas for all 2nd dimension modulated peaks corresponding to some analyte. However, this is a cumbersome task certainly unfit for regular applications. Therefore, a data-processing approach providing both multivariate processing for quantitative analysis as well as retention information on 1st and 2nd dimensions for the target analytes would be interesting. In this paper we propose the use of a new chemometric tool – Interval Partial Least Squares (iPLS) regression applied to GC×GC-FID data to perform this task. Partial least squares (PLS) regression is a method for building regression models between independent (x) and dependent (y) variables. However, a sub-set of the data may result on more reliable models: this is the reasoning of interval partial least square (iPLS). iPLS splits the raw second-order data set (Signal × ¹t_R × ²t_R tensor) in intervals in both dimensions and calculates NPLS (N-way Partial Least Squares) models for each reduced matrix (which are related to individual analytes, hinting their retention on ¹t_R × ²t_R plan). This method was evaluated on the detection and quantitation of selected allergenics in perfume samples. A lab-made GC×GC-FID based on a cryogenic modulator was employed; for all analyses, a HP-5 (30 m x 0.25 mm x 0.25 μm) + DB-Wax (0.9 m x 0.1 mm x 0.1 mm) was used. The relevant operational conditions were: T_{inj} = T_{det} = 250 °C; T_{col} = 3 min @ 60 °C → 3 °C min⁻¹ → 5 min @ 240 °C; carrier gas = H₂ @ 0.6 mL min⁻¹; split injection (1 μL with SR = 1:20) and P_M = 4.0 s. Preliminary studies were performed using synthetic mixtures resembling the samples (0.0 and 3.0 % v/v ethanol solutions of 1-octanol, undecane, 2-octanone, ciclohexanone and toluene). The results were compared to NPLS using the whole chromatograms without interval selection. For all compounds, the iPLS was able to locate the correct region on the two-dimensional chromatograms corresponding to the target peaks, also providing root mean square errors of cross-validation (RMSECV) values was lower than the NPLS. This approach was further applied to the quantification of three allergenics (geraniol, citronellol and benzyl alcohol) in perfume samples - low price replacements for brand name perfumes, widely available on the local market - by GC×GC-FID. The samples were diluted with ethanol (1:4) and spiked with the analytes, resulting on concentrations up to 100 ppm. The RMSECV obtained with iPLS were 9.75, 9.49, and 12.67 %, while the RMSECV obtained for NPLS was 40.41, 49.47 and 39.62 % for geraniol, citronellol and benzyl alcohol, respectively. These results point that iPLS can be a powerful tool both for quantitative and qualitative analysis using GC×GC data.

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